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Characterization of methyl bromide and methyl chloride fluxes at temperate freshwater wetlands

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[1] Methyl bromide (CH_3Br) and methyl chloride (CH_3Cl) are important natural sources of halogens to the atmosphere. A total of 568 CH_3Br and 418 CH_3Cl net flux measurements were made for up to 2 years at the same locations within four different wetlands in Scotland. Mean (± 1 standard deviation (SD)) CH_3Br and CH_3Cl net fluxes across all measurements at each wetland were: Auchencorth Moss, $8 (\pm 7)$ and $3560 (\pm 1260) \text{ ng m}^{-2} \text{ h}^{-1}$; Old Castle Farm, $420 (\pm 70)$ and $500 (\pm 260) \text{ ng m}^{-2} \text{ h}^{-1}$; Red Moss of Balerno, $500 (\pm 90)$ and $140,000 (\pm 36,000) \text{ ng m}^{-2} \text{ h}^{-1}$; and St Margaret's Marsh, $3600 (\pm 600)$ and $-270 (\pm 450) \text{ ng m}^{-2} \text{ h}^{-1}$. None of the wetlands was a large net sink. Where substantial emissions were observed, these followed seasonal trends, increasing early in the growing season and declining in early autumn. Some diurnal cycles were observed, with emissions greatest during the day, although lower emissions were present at night. None of the measured environmental parameters was a strong “universal” driver for fluxes, which were heterogeneous within and between the wetlands, and larger on average than reported to date; plant species appeared to be the dominant factor, the latter confirmed by vegetation removal experiments. *Calluna vulgaris* and *Phragmites australis* emitted particularly large amounts of CH_3Br , the former also emitting substantial CH_3Cl . While acknowledging the substantial uncertainties in extrapolating globally, observations from this work suggest that wetlands contribute more CH_3Br and CH_3Cl to the atmosphere than current World Meteorological Organization estimates.

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1. Introduction

[2] Methyl bromide (CH_3Br) and methyl chloride (CH_3Cl) are two halogen-containing compounds with significant roles in stratospheric ozone destruction, but predominantly natural sources. These include oceans and biomass burning (which can also be anthropogenic) for both gases, and tropical ecosystems for CH_3Cl [World Meteorological Organization (WMO), 2011]. The major sinks of CH_3Br and CH_3Cl are oceans, soils, reaction with OH radical in the troposphere, and photolysis [WMO, 2011]. CH_3Cl is the most abundant Cl-containing organic compound in the atmosphere (2008 global mixing ratio 545 parts per trillion by volume (pptv)) and is estimated to contribute 16% of the total Cl (from long-lived gases) to the atmosphere [WMO, 2011]. Although CH_3Br has lower atmospheric abundance (2008 global mixing ratio 7.3 parts per trillion (ppt) [WMO, 2011]), release of a Br atom is more destructive to stratospheric ozone than

Cl. In accordance with the Montreal Protocol and subsequent amendments, anthropogenic sources of both gases are being phased out so the relative importance of the contribution of Cl and Br to the stratosphere from natural CH_3X sources is increasing [WMO, 2011]. This is particularly so for CH_3Br , which has large anthropogenic sources in addition to natural sources [WMO, 2011]. (In the rest of this paper the term CH_3X is used as shorthand for CH_3Br and CH_3Cl together.)

[3] Despite the significance of CH_3X in the atmosphere, their global budgets remain highly uncertain because of the intrinsic difficulty in obtaining and extrapolating flux estimates from temporally and spatially representative field data in diverse ecosystems. For CH_3Br , in particular, estimates of global sinks (148 Gg yr^{-1}) remain significantly unbalanced by $\sim 30\%$ with estimates of global sources (112 Gg yr^{-1} [WMO, 2011]). Discrepancies are less acute for CH_3Cl within its estimated global annual flux turnover of $\sim 4100 \text{ Gg yr}^{-1}$. The current World Meteorological Organization (WMO) estimates for peatland sources are 48 Gg yr^{-1} ($\sim 1.2\%$ of natural sources) for CH_3Cl [WMO, 2007] and 0.6 Gg yr^{-1} ($\sim 0.7\%$ of natural sources) for CH_3Br [WMO, 2011], the latter a significant downward revision from the WMO [2007] value of 4.6 Gg yr^{-1} . For both gases the global estimates are derived from measurements in just two locations, New Hampshire (USA) peatlands [White *et al.*, 2005] and Irish peatlands [Dimmer *et al.*, 2001]. There are no CH_3X measurements in natural non-peat-based wetlands.

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Consequently, the overarching aim for this work was to characterize CH_3X fluxes in temperate wetland ecosystems in order to help refine the CH_3X global budgets. The two motivations were: (1) CH_3X fluxes in temperate freshwater wetlands have not been studied in spatial and temporal detail; (2) wetland area is subject to change—both reduction through drainage and increase through rejuvenation of previously drained wetland for aesthetic or conservation purposes [Burn and Diack, 2008].

[4] Emission of CH_3X in natural ecosystems is generally thought to arise from methyl transferase activity in plants [Attieh *et al.*, 1995; Rhew *et al.*, 2003] and fungi [Harper *et al.*, 1990; McNally *et al.*, 1990; Harper *et al.*, 1991; McNally and Harper, 1991]. Variable methyl transferase activity among plant species [Saini *et al.*, 1995] suggests that the magnitude of CH_3X emissions will vary with plant species and this is the case in Californian grasslands [Rhew and Abel, 2007], Irish peatlands [Dimmer *et al.*, 2001], and Californian and Scottish saltmarshes [Manley *et al.*, 2006; Blei *et al.*, 2010b]. Laboratory studies have also implicated abiotic routes to CH_3X production in soils [Keppler *et al.*, 2000]. A soil sink, which has been more comprehensively studied for CH_3Br than for CH_3Cl , has been documented across a wide range of soil types [Hines *et al.*, 1998; Serça *et al.*, 1998; Shorter *et al.*, 1995; Varner *et al.*, 1999b]. Although most studies measure only net CH_3X flux, the presence of known source and sink processes for CH_3X across a wide range of natural ecosystems suggests that CH_3X uptake and emission can occur simultaneously within an ecosystem. Isotope tracer experiments have demonstrated this to be the case for tundra [Teh *et al.*, 2009], grasslands [Rhew and Abel, 2007; Teh *et al.*, 2008; Rhew, 2011], and saltmarshes [Rhew and Mazéas, 2010]. However, with their intrinsically high water table, wetlands are not expected to be globally significant sinks of CH_3X .

[5] Few data sets have sufficient temporal resolution to identify seasonal and diurnal trends in CH_3X fluxes. Clear seasonal trends have been observed at Scottish saltmarshes [Drewer *et al.*, 2006; Blei *et al.*, 2010b], New Hampshire wetlands [White *et al.*, 2005], and Californian rice paddies [Redeker and Cicerone, 2004]. In the saltmarshes and rice paddies CH_3Br emission rates broadly corresponded to seasonal trends in plant growth, air temperature and light intensity, indicative of a biologically-mediated process. Diurnal measurements have been made in Scottish saltmarshes [Drewer *et al.*, 2006; Blei *et al.*, 2010b], temperate woodland leaf litter [Dimmer *et al.*, 2001; Drewer *et al.*, 2008], temperate coastal marsh [Dimmer *et al.*, 2001], temperate peatlands [Dimmer *et al.*, 2001], Californian saltmarshes [Rhew *et al.*, 2002], high-latitude wetlands [Hardacre *et al.*, 2009], tropical forests [Blei *et al.*, 2010a], and from two tropical fern species (*Cyathea podophylla* and *Cyathea lepifera*) [Saito and Yokouchi, 2006]. Of these, diurnal variation in CH_3Br flux was observed at Scottish saltmarshes, certain temperate woodland leaf litter sampling points, high-latitude wetlands, temperate peatlands, Californian saltmarshes, the tropical ferns and some tropical plant species. Diurnal variation in CH_3Cl flux was observed at temperate coastal marsh, temperate woodland leaf litter, Californian saltmarshes and from certain tropical plant species. Where diurnal cycles in CH_3X emission rates were observed these were at sampling points that

enclosed vegetation and generally continued into the night, albeit at a lower rate.

[6] In this work, CH_3X fluxes were measured at five different temperate peat and nonpeat wetland ecosystems commonly found in the UK. Individual sampling points were chosen to capture variation in vegetation and hydrology within each wetland. At four of the wetlands, measurement of CH_3X fluxes was undertaken at all sampling points for up to 2 years to investigate seasonality. Diurnal trends were also investigated.

2. Methods

2.1. Wetland Site Descriptions

[7] The majority of flux measurements were made at four wetlands in eastern Scotland, UK, which represented the following different types of temperate wetland (described below and in Table 1): peatland, *Phragmites australis* reed bed, and agricultural wetland. At each wetland CH_3X fluxes were measured from fixed sampling points sited to capture differences in the vegetation, hydrology, and microtopography of the wetland. Fluxes were measured approximately every 2 weeks at each sampling point, from June 2007 to July 2009 for CH_3Br , and from January 2008 to July 2009 for CH_3Cl (exact dates varied slightly), yielding ~27 and ~19 values of CH_3Br and CH_3Cl fluxes, respectively, per individual sampling point.

[8] Auchencorth Moss (ACM) is a blanket peat bog (~9.64 km²) situated southwest of Edinburgh (55°46'N 3°16'W, 265 m above sea level (a.s.l.)). A combination of drainage and grazing means this site is not in a fully natural peat bog state. The hummock-hollow microtopography at ACM, predominantly *Sphagnum* spp., other bryophytes, grasses, and sedges, was interspersed with patches of soft rush (*Juncus effusus*). The site slopes down on two sides to form a shallow “V” in which there is a stream. The four sampling points at ACM comprised two in the lower part of the bog close to the stream and two in the higher part of the bog. The water table at the four sampling points was generally between 0 and 100 mm below the surface but could be 300 mm below the surface in summer.

[9] Old Castles Farm (OCF) is a small semi-natural, constructed wetland (~7500 m²) situated approximately 70 km east of Edinburgh (55°49'N 2°13'W, 65 m a.s.l.). Four sampling points at OCF captured the main types of vegetation present: common reed (*Phragmites australis*), soft rush (*Juncus effusus*), reed sweetgrass (*Glyceria maxima*), and hairy bitter cress (*Cardamine hirsute*). A fifth sampling point was a mixture of *Glyceria maxima*, common nettle (*Cirsium arvense*), and creeping thistle (*Urtica dioica*).

[10] Red Moss of Balerno (RMB) is a raised peat bog (~15.7 ha), located 15 km southwest of Edinburgh (55°51'N 3°20'W, 240 m a.s.l.), with well-defined hummock-hollow microtopography. The site is undergoing restoration, but due to past drainage and peat extraction water levels are not currently high enough for peat accumulation. RMB has an ombrotrophic dome that is characteristic of raised peat bogs and minerotrophic surrounding areas. Initially, four sampling points were established at RMB, two each in the ombrotrophic and minerotrophic areas. These four sampling points predominantly enclosed ling heather (*Calluna vulgaris*). To compare these sampling points with areas not covered by *C. vulgaris*,

Table 1. Mean (± 1 SD) CH_3Br and CH_3Cl Fluxes From Individual Sampling Points^a

Sampling Point	Mean CH_3Br flux / $\text{ng m}^{-2} \text{h}^{-1}$ (± 1 SD)	Mean CH_3Cl Flux / $\mu\text{g m}^{-2} \text{h}^{-1}$ (± 1 SD)	Predominant Vegetation ^b (%)	Soil $[\text{Br}^-]$ & $[\text{Cl}^-]$ / mg kg^{-1}	Soil Moisture / %	Soil pH	Soil OM / %	CH_3Br Flux / $\text{ng g}^{-1} \text{dwt h}^{-1}$	CH_3Cl Flux / $\text{ng g}^{-1} \text{dwt h}^{-1}$
ACM1	0 \pm 40	-0.38 \pm 2.00	<i>Juncus effusus</i> (67%) <i>Pleurozium schreberi</i> (25%)	<lod & 311	93	4.3	83	0.0 \pm 0.04	19.8 \pm 9.6
ACM 2	-20 \pm 30	1.14 \pm 2.94	<i>Polytrichum commune</i> (48%) <i>Hylocomium splendens</i> (28%) <i>Carex nigra</i> (12%)	<lod & 320	90	4.4	87	0.0 \pm 0.03	0.0 \pm 11
ACM 3	-20 \pm 30	-0.29 \pm 0.94	<i>Festuca ovina</i> (8%) <i>Hylocomium splendens</i> (67%) <i>Carex nigra</i> (13%)	<lod & 95	81	4.4	72	0.0 \pm 0.03	62.1 \pm 9.5
ACM 4	64 \pm 100	13.7 \pm 17.6	<i>Juncus effusus</i> (33%), <i>Pleurozium schreberi</i> (49%), <i>Polytrichum commune</i> (9%)	<lod 80	73	4.9	34	0.32 \pm 0.16	0.0 \pm 8.0
OCF1	260 \pm 200	0.28 \pm 0.70	<i>Glyceria maxima</i> (100%)	<lod & 27	63	6.9	11	0.69 \pm 0.09	—
OCF2	560 \pm 700	-0.38 \pm 1.31	<i>Glyceria maxima</i> (73%) <i>Cirsium arvense</i> (19%)	<lod & 90	36	6.2	10	2.14 \pm 0.09	—
OCF3 ^c	180 \pm 280	1.07 \pm 2.44	<i>Urtica dioica</i> (7%)	— & —	—	—	—	4.96 \pm 0.99	—
OCF4	220 \pm 280	0.62 \pm 3.78	<i>Cardamine hirsute</i> (100%)	<lod & 28	51	6.8	11	0.0 \pm 0.18	—
OCF5	900 \pm 1310	0.96 \pm 2.95	<i>Phragmites australis</i> (100%)	<lod & 30	53	6.7	15	0.0 \pm 0.45	—
RMB1	1550 \pm 1640	550 \pm 740	<i>Calluna vulgaris</i> (green, 83%) <i>Calluna vulgaris</i> (brown, 17%)	<lod & 64	88	3.7	98	0.56 \pm 0.18	28.5 \pm 2.8
RMB2	300 \pm 360	14 \pm 90	<i>Calluna vulgaris</i> (green, 45%) <i>Calluna vulgaris</i> (brown, 12%)	<lod & 64	88	3.7	98	0.0 \pm 0.18	14.7 \pm 6.2
RMB3	680 \pm 910	150 \pm 170	<i>Eriophorum angustifolium</i> (41%) <i>Calluna vulgaris</i> (green 91%)	<lod & 120	92	3.8	92	0.26 \pm 0.14	131 \pm 5
RMB4	0 \pm 10	3 \pm 4	<i>Eriophorum angustifolium</i> (6%) <i>Polytrichum commune</i> (16%)	<lod & 62	84	3.8	81	0.0 \pm 0.12	1.9 \pm 1.1
RMB5 ^c	10 \pm 40	-1 \pm 2	<i>Eriophorum angustifolium</i> (12%) <i>Sphagnum cuspidatum</i> (71%)	— & —	—	—	—	0.0 \pm 0.41	-10.5 \pm 3.6
RMB6 ^c	150 \pm 255	30 \pm 100	<i>Eriophorum angustifolium</i> (98%) <i>Calluna vulgaris</i> (green 37%)	— & —	—	—	—	0.0 \pm 0.15	253 \pm 5
RMB7 ^c	0 \pm 10	3 \pm 4	<i>Vaccinium myrtillus</i> (55%), <i>Hypnum julidicum</i> (6%)	— & —	—	—	—	0.0 \pm 0.16	11.4 \pm 5.7
RMB8 ^c	-10 \pm 20	0 \pm 0	<i>Eriophorum angustifolium</i> (37%) <i>Pleurozium schreberi</i> (60%)	— & —	—	—	—	0.0 \pm 0.09	0.0 \pm 0.8
SMM1 ^d	2460 \pm 4200	0.97 \pm 4.17	<i>Pleurozium schreberi</i> (31%) <i>Vaccinium myrtillus</i> (65%)	63 & 19900	60	7.3	20	12.0 \pm 0.11	2.9 \pm 2.4
SMM2 ^d	2240 \pm 2970	-0.98 \pm 4.34	<i>Phragmites australis</i> (100%)	49 & 14800	64	7.4	22	4.01 \pm 0.18	0.0 \pm 2.0
SMM3	6020 \pm 8990	0 \pm 3.20	<i>Phragmites australis</i> (100%)	<lod & 650	39	8.5	47	1.95 \pm 0.14	2.0 \pm 0.9
SMM4	3130 \pm 4530	-0.98 \pm 3.51	<i>Phragmites australis</i> (100%)	<lod & 550	39	8.4	14	2.02 \pm 0.12	0.0 \pm 1.1

^aAt Auchencorth Moss (ACM), Old Castles Farm (OCF), Red Moss of Balerno (RMB) and St. Margaret's Marsh (SMM) Wetlands. Also included are the predominant vegetation and soil data for each enclosure, and CH_3X flux per dry mass of above-ground vegetation present at the final flux measurement. Because only one determination is available for each of these latter fluxes, the uncertainties presented are the analytical uncertainties in the individual measurement.

^bAll vegetation at the wetlands is natural to the UK.

^cSoil property data were not available for OCF3 or RMB5-8, and CH_3Cl fluxes normalized to biomass were not available for the OCF sampling site because of instrumentation issues.

^dSMM1 and SMM2 were situated in the wetter eastern end of the marsh where the water table was higher. In addition, this (lower) part of the marsh was sometimes inundated with sea-water during combinations of storm conditions and high tides.

“—” Indicates that no data were obtained.

four more sampling points were subsequently installed from September 2008 (again two each in the ombrotrophic and minerotrophic areas).

[11] St Margaret's Marsh (SMM) is a *Phragmites australis* wetland (~9.16 ha) located on the north bank of the Forth estuary (56°01'N 3°24'W, 0 m a.s.l.). The western end of the reed bed is drier and divided from the wetter eastern end by a raised bank. Of four sampling points at SMM, two each were in the drier and wetter areas of the reed bed. SMM was uniformly covered by *P. australis* although the size of the plants was variable.

[12] Additional measurements of CH₃X flux were made at a second *P. australis* wetland at Caerleverock (CLR) wetland situated on the Solway Firth in southwest Scotland. The main freshwater wetland areas at CLR encompass 32 ha and were created by the construction of a sea wall in 1840, but are subject to occasional salt-water inundation. Stands of *P. australis* in the wetland are occasionally subject to controlled cutting as part of habitat management. On four separate occasions between August 2007 and July 2009 flux measurements were made at four locations within the main freshwater wetland. Three sampling points contained only *P. australis* vegetation, the fourth was in a dry area and contained grasses in addition to *P. australis*. The same sampling method was employed at CLR as at the other wetlands except that the four sampling points at CLR were not fixed, although as close to the same location as possible on each visit. In addition, extra enclosures in other parts of the reed bed were performed on each visit, but these differed between visits in order to investigate spatial variation.

2.2. Sampling Methods

[13] Field measurements were similar to those described in Blei *et al.* [2010b]. At each sampling point a 400 mm diameter by 200 mm high PVC collar was sunk 150 mm into the ground and left permanently in place. For net flux determination, an appropriately-sized chamber made of 0.5–1.0 mm translucent polythene (typical transmission of photosynthetically active (PAR) radiation ≈ 85%) was secured to the collar to create an airtight enclosure. A 0.044 m³ chamber was used at most sampling points. Chambers of 0.18 and 0.28 m³ were used at SMM sampling points and certain OCF sampling points where vegetation was higher. Chambers were sealed for 10 min after which a 500 mL sample was withdrawn by gas-tight syringe and transferred to an evacuated 1 L Tedlar bag (SKC, PA, USA). An ambient air sample was collected from ~1 m above the ground. Air temperature, subsurface temperature at 50 mm depth, and internal chamber temperature were measured during each sample collection. Total solar radiation and PAR were also recorded. In using a single-chamber sample, albeit with short (10 min) enclosure, there are acknowledged trade-offs between (a) the ability to collect a greater number of samples in order better to characterize the temporal and spatial flux variability, (b) uncertainty at high emitting sites because $t=0$ concentrations at chamber enclosure may be elevated compared with the 1 m background sample (leading to net flux overestimation), (c) limiting stress to the enclosed plants, and (d) allowing sufficient CH₃X to accumulate in the chamber for flux determination.

[14] For investigation of diurnal trends, CH₃X fluxes were measured approximately every 4 h over a 24 h period in summer at all sampling points at each wetland (ACM,

11–12 August 2008; OCF, 5–6 August 2008; RMB, 15–16 August 2008; SMM, 8–9 August 2008). CH₃X fluxes were also measured at RMB between 07:00 and 17:00 (winter daylight hours) on 17 February 2009 as this wetland also remained active for CH₃X fluxes over winter.

2.3. Vegetation Removal Experiment

[15] On completion of the time series of flux determinations, all the above-ground vegetation was removed from all of the sampling points at ACM (22 June 2009), OCF (11 June 2009), RMB (9 July 2009), and SMM (7 July 2009) to (a) determine the species and mass composition of the enclosure vegetation and (b) investigate the impact on fluxes of vegetation removal. Live (green) vegetation was sorted by species and dried at 70 °C until constant mass. CH₃X fluxes were measured before, immediately, and 2 weeks after vegetation removal. Any new above-ground vegetation growth was removed before enclosure at the postremoval sampling.

2.4. CH₃X Analytical Methods

[16] Air samples were analyzed for CH₃Br and CH₃Cl using an HP5890 gas chromatograph with a custom-built two-stage preconcentration unit, a ZB642 capillary column (Phenomnexus Inc., Torrance, CA, USA, 30 m length, 0.32 mm internal diameter, 1.8 µm film thickness), and oxygen-doped electron capture detection [Hardacre *et al.*, 2009; Blei *et al.*, 2010b]. The first trap was a one-fourth-inch diameter by 100 mm long stainless steel tube filled with Tenax TA 60/80 mesh (Supelco, Bellefonte, PA, USA) cooled to –30 °C before loading using dual two-stage Peltier cells (Melcor, Trenton, NJ, USA). The second trap was a one-eighth-inch diameter by 200 mm long stainless steel tube filled with fine glass beads and cooled to –80 °C using dry ice. A 100 mL sample aliquot was passed through the first trap and the trapped analytes subsequently transferred to the second trap using switching valves (VICI, Houston, TX, USA). After 5 min the second trap was flash heated to transfer the analytes onto the column. The temperature program was 5 min at 40 °C, ramping for 5 min at 40 °C min^{–1} and hold for 5 min at 240 °C.

[17] Calibration curves for CH₃Br and CH₃Cl were prepared weekly using dilutions of certified standards: 500 ± 10 ppbv CH₃Br in nitrogen (Air Products Inc.) and 15.8 ± 0.5 ppmv CH₃Cl in nitrogen (Air Liquide). Low (10 pptv) and high (100 pptv) standards were analyzed 1–3 times per batch of samples to identify and correct for any significant variation in response.

[18] To calculate a final net flux first requires the CH₃X mixing ratio in the background sample to be subtracted from the mixing ratio of an enclosure sample. Identified sources of uncertainty in mixing ratio quantification include the certified gas standard mixing ratio, dilution of the certified standard to the working standard, variation in analyte transfer to the GC, and integration of the CH₃X peak in the chromatogram. With the exception of the uncertainty in the certified CH₃X standards, these uncertainties are random and are incorporated within the uncertainty derived from interpolation of the standard calibration constructed for a given analytical run. The uncertainty in the certified standards is explicitly added to the uncertainty in the GC analysis and the “analytical uncertainty” determined by combining the described uncertainties using standard propagation of errors.

[19] The limit of detection (lod) for a net flux was defined by the CH_3X mixing ratio of an enclosure sample being significantly different from the CH_3X mixing ratio of the corresponding background air sample. The lod was defined here as 1.96 times the analytical uncertainty in the background sample. The average lod for discrimination of significant difference between sample and background mixing ratios was 8 ppt CH_3Br and 360 ppt CH_3Cl , corresponding to net fluxes of $70 \text{ ng m}^{-2} \text{ h}^{-1}$ and $1600 \text{ ng m}^{-2} \text{ h}^{-1}$ for CH_3Br and CH_3Cl , respectively, for the normal enclosure chamber used.

2.5. Soil Analytical Methods

[20] Samples of soil were collected on 11 October 2007 (ACM and OCF) and 18 October 2007 (RMB and SMM). At each sampling point at each field site six replicate soil cores from 0–100 mm depth were taken using a 30 mm diameter screw auger at evenly spaced points 0.5 m outside the sampling collar. The six replicates from each location were combined in the laboratory to form a mixed bulk sample and then passed through a 2 mm diameter sieve to remove larger plant and stony material. The soils were stored at 4°C until analysis.

[21] For soil gravimetric water content, triplicates of 10 g of soil from each sampling point were precisely weighed into a ceramic crucible and dried at 105°C until constant mass. Water content was expressed as percentage water content relative to mass of fresh soil. Soil organic matter content was determined via loss on ignition. The triplicates of dried soil samples were transferred to a muffle furnace and heated at 500°C for 12 h. The cooled sample was reweighed and organic content as mass lost by ignition expressed relative to the soil dry mass.

[22] For soil pH determination, duplicates of approximately 20 g of fresh soil were weighed into a glass sample jar and 50 mL of reverse osmosis water was added. The mixture was stirred vigorously for 30 s and the suspension allowed to settle for 30 min. The pH was measured using a calibrated pH probe (Hanna Instruments, RI, USA).

[23] For soil halide ion (Cl^-/Br^-) concentration, approximately 10 g of fresh soil was precisely weighed into a plastic container and 100 mL of deionized water added. The mixture was shaken for 1 h with a wrist action shaker (Secor Scientific Instruments Ltd., India) and the suspension allowed to settle. The extractant was filtered through Whatman No. 1 filter paper and the filtrate was stored at 4°C until analysis for Br^- and Cl^- using a DX-500 ion chromatograph (DIONEX, Sunnyvale, CA, USA). Separation was achieved using an IonPac AS22A analytical column and a mobile phase composed of 4.5 mM sodium bicarbonate and 1.4 mM sodium carbonate delivered at a flow rate of 1.2 mL min^{-1} . The lods for Br^- and Cl^- were 0.02 mg L^{-1} and 0.01 mg L^{-1} , respectively. Each soil sample was analyzed in duplicate. The halide ion concentration was expressed relative to soil dry mass.

3. Results and Discussion

3.1. CH_3Br and CH_3Cl Fluxes and Their Seasonal Trends

[24] A total of 568 CH_3Br and 418 CH_3Cl net flux determinations were made across the different sampling points of the wetlands over the 2 year duration of this study. The full time series of net CH_3Br and CH_3Cl fluxes at each

sampling point within the four principal wetlands investigated are shown in Figure 1. The long-term mean fluxes at each individual sampling point in each wetland are given in Table 1. The overall long-term mean (± 1 SD) net fluxes from all measurements made at each wetland are: ACM (Auchencorth Moss), $8 (\pm 7) \text{ ng CH}_3\text{Br m}^{-2} \text{ h}^{-1}$ and $3560 (\pm 1260) \text{ ng CH}_3\text{Cl m}^{-2} \text{ h}^{-1}$; OCF, $420 (\pm 70) \text{ ng CH}_3\text{Br m}^{-2} \text{ h}^{-1}$ and $500 (\pm 260) \text{ ng CH}_3\text{Cl m}^{-2} \text{ h}^{-1}$; RMB, $500 (\pm 90) \text{ ng CH}_3\text{Br m}^{-2} \text{ h}^{-1}$ and $140,000 (\pm 36,000) \text{ ng CH}_3\text{Cl m}^{-2} \text{ h}^{-1}$; SMM, $3600 (\pm 600) \text{ ng CH}_3\text{Br m}^{-2} \text{ h}^{-1}$ and $-270 (\pm 450) \text{ ng CH}_3\text{Cl m}^{-2} \text{ h}^{-1}$. These data show that different wetland systems contribute widely varying amounts of CH_3Br and CH_3Cl to the atmosphere. Overall, RMB was the greatest net emitter of CH_3Br and CH_3Cl . OCF and ACM were, respectively, the smallest net emitters of CH_3Cl and CH_3Br .

[25] Seasonal trends in CH_3X emissions that approximately followed the Scottish growing season and associated trends in temperature (air and soil), PAR, and plant growth cycles were observed at most of the individual sampling points in this study (Figure 1). The growing season is defined here as beginning when mean daily air temperature exceeds 5°C for five consecutive days and ending when mean daily temperature is below 5°C for five consecutive days. For eastern Scotland the growing season extends for ~240 days from the end of March to mid-November [Adams and Early, 2004]. CH_3X fluxes at sampling points where clear seasonal trends were not observed (CH_3Cl fluxes from all SMM sampling points, CH_3Cl fluxes at OCF1, OCF2, and OCF5, and CH_3Cl fluxes at ACM1, ACM2, and ACM3) were generally small, fluctuating between emission and uptake. Maximum net CH_3Br and/or CH_3Cl emissions were observed within the period of maximum summer air temperature, soil temperature, and PAR intensity. At the beginning of the growing season, net emissions were observed after air temperature, soil temperature, and PAR began to increase, which was from around mid-April. Peak emissions were generally observed in early summer (June–July). In addition to temperature and PAR, seasonal trends in CH_3X emission may also be linked to (a) plant biomass, which is at a minimum (or absent) during the winter months, rapidly increases at the start of the growing season and peaks at the end of the growing season, or (b) stages of the plant growth cycle, as observed for CH_3X emissions from rice paddies [Redeker et al., 2004]. The observation of seasonal trends in CH_3X emissions at Scottish wetlands is consistent with other long-term measurements at temperate peatlands [White et al., 2005] and saltmarshes [Drewer et al., 2006; Blei et al., 2010b].

[26] Comparatively large CH_3Br and CH_3Cl net emissions were also observed throughout the winter at RMB sampling points RMB1–3. Significant winter emissions of CH_3X from wetlands (or any other ecosystem) have not previously been reported (but are infrequently investigated) and are an important consideration for global scale-up. Unique to sampling points RMB1–3 was the predominant *Calluna vulgaris* vegetation, which is perennial, evergreen, and woody. Unlike sampling points that enclose annual species (e.g., *P. australis* sampling points at SMM) or perennial non-woody species (e.g., sampling points at OCF, ACM, and RMB4), which did not emit CH_3X during winter (Figure 1), a relatively large amount of biomass was present at RMB1–3 during the winter. Although *C. vulgaris* did not emit large

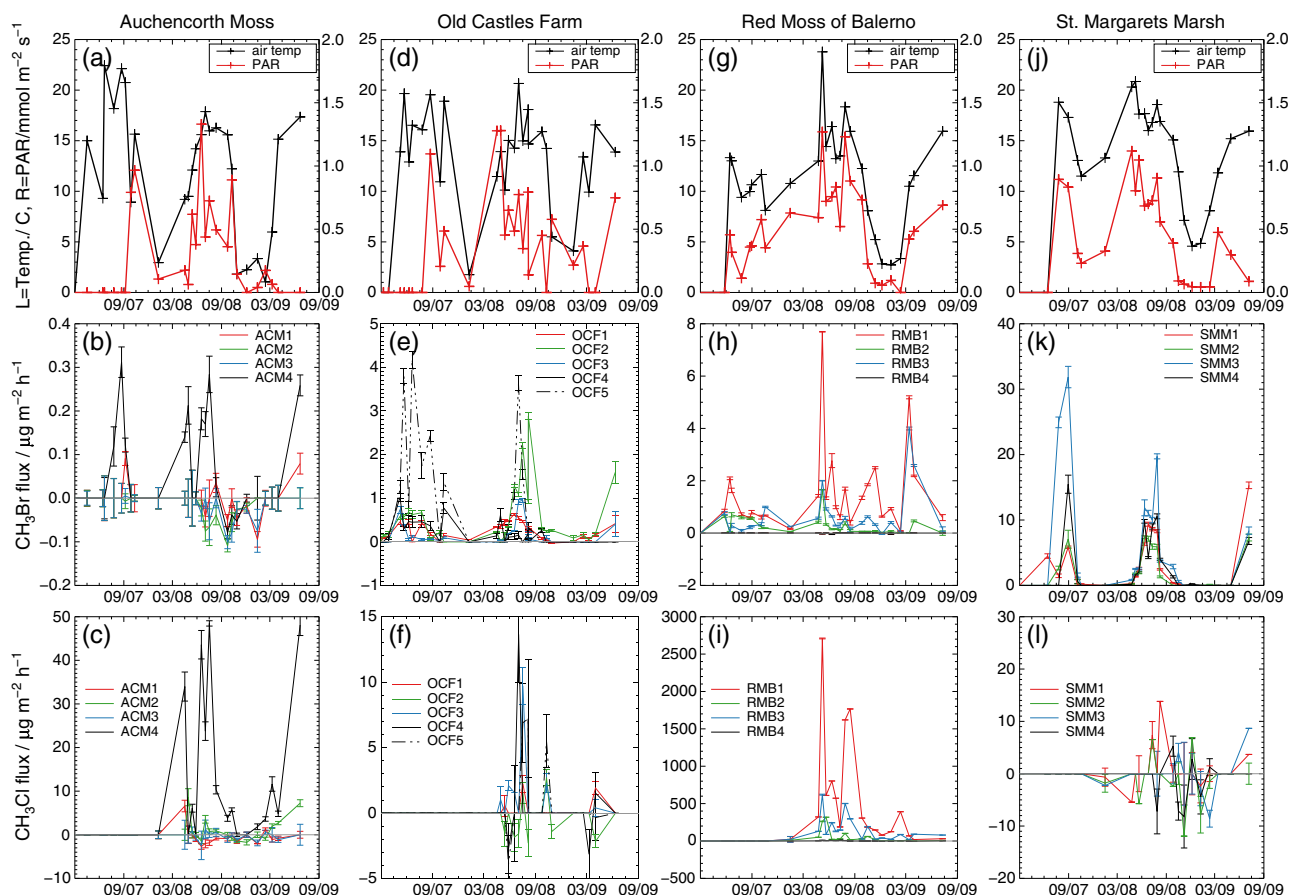


Figure 1. Air temperature, PAR, and methyl halide net fluxes at Auchencorth Moss (ACM), Old Castles Farm (OCF), Red Moss of Balerno (RMB), and St. Margaret's Marsh (SMM) wetlands. (a, d, g, j) Temperature and PAR data (averaged for the sampling time at each site on the day of sampling); (b, e, h, k) CH_3Br fluxes and (c, f, i, and j) CH_3Cl fluxes. Vertical bars show ± 1 SD of the analytical uncertainty associated with each CH_3X measurement. Zero flux lines are plotted in gray. Dates are presented in mm/yy format.

amounts of CH_3X per unit biomass (Table 1), the presence of a comparatively large amount of biomass in winter maintained significant CH_3X flux per unit area. Abiotic soil-based production of CH_3X in low pH conditions has also been proposed [Keppler *et al.*, 2000] and the low pH (~3.8) of the peat at RMB could be a suitable environment for these reactions. However, vegetation removal experiments in the summer months (see section 3.3) did not provide supporting evidence for an important soil abiotic CH_3X source at RMB or any of the wetland sites in this study, indicating that the winter emissions are likely of plant origin.

[27] None of the wetlands in this study were a large net sink for CH_3X , although net uptake of CH_3Br and/or CH_3Cl was observed at some time at most of the wetlands (Figure 1). Seasonality in net CH_3Br uptake was observed only at ACM. Net uptake of CH_3Cl was observed at OCF and SMM. Seasonal CH_3X uptake at ACM and SMM began late in the growing season and continued into winter, in contrast to net CH_3X emissions, which occurred during the growing season.

[28] Evidence for bidirectional uptake and emission was observed at ACM2 and ACM4 for CH_3Cl and CH_3Br , respectively. At these two sampling points, net CH_3X emission switched to net CH_3X uptake at the end of the growing season

and vice versa at the start of the growing season. The observation of bidirectional uptake and emission in this study is consistent with studies at temperate grasslands [Rhew and Abel, 2007] and peatlands [White *et al.*, 2005]. It is likely that uptake and emission occurred concurrently at many of the sampling points in this study, but with uptake generally masked by larger emissions. Individual sampling points at each wetland that were a net sink of CH_3X over the whole period of measurement can be noted from Table 1.

3.2. Diurnal Trends in CH_3X Fluxes

[29] The subdiurnal measurements of net flux at each wetland are shown in Figure 2, averaged across all sampling locations at each wetland. Daily trends were less well-defined than annual trends, although diurnal measurements were only made once at each location. CH_3Br and CH_3Cl emissions from SMM (Figure 2d), CH_3Br emissions from RMB (Figure 2c), and to a lesser extent CH_3Cl uptake at OCF (Figure 2b), followed a clear pattern that matched the daily cycle in PAR and air temperature. Maxima in fluxes (generally emissions) were observed during the warmest and lightest part of the day and mean net emissions decreased by approximately a factor of three during the night. CH_3X fluxes did not follow daily PAR and temperature

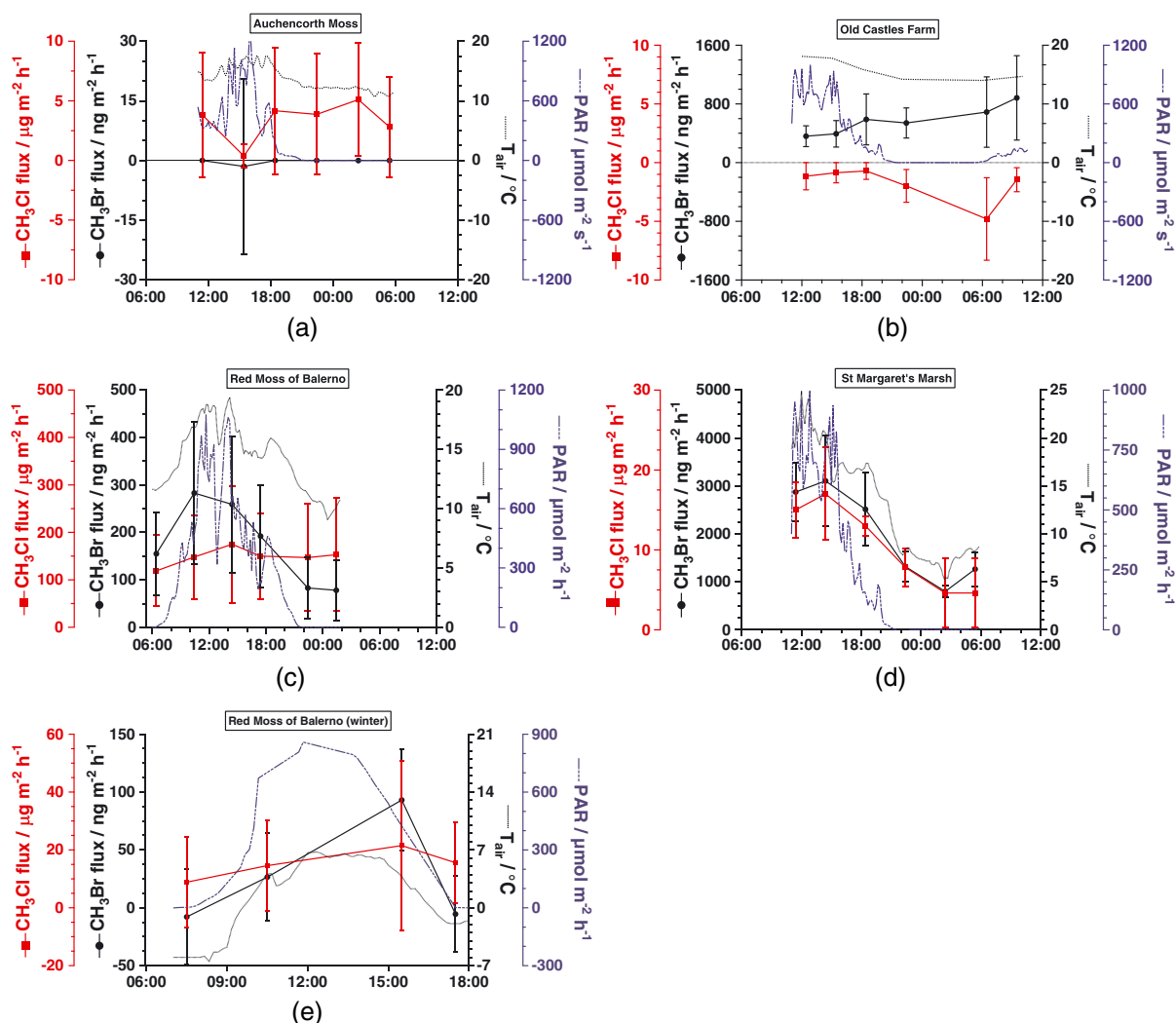


Figure 2. Summer-time diurnal net CH_3Br and CH_3Cl fluxes at (a) ACM, (b) OCF, (c) RMB, and (d) SMM. (e) CH_3Br and CH_3Cl fluxes measured during a 12 h period in winter at RMB. Note the different time scale for Figure 2e. Vertical bars show ± 1 SD about the mean flux from all sampling points in the wetland on the given sampling occasion. Air and soil temperatures and PAR intensity on each sampling occasion are also shown.

cycles at either OCF or ACM (except perhaps for CH_3Cl at OCF, as noted above). No CH_3Br fluxes were observed at ACM during these measurements (Figure 2a), consistent with the long-term observations, which showed that seasonal CH_3Br emissions at ACM were decreasing by mid-August, when the diurnal measurements were made (Figure 1b). CH_3Cl uptake was observed at OCF (Figure 2b). However, in general, the CH_3X fluxes at the ACM and OCF wetlands were constant during the day of measurement.

[30] As noted above, the RMB site was the only wetland in this study to show persistent CH_3X emission fluxes during winter. Figure 2e shows that net emissions of CH_3Br occurred at 10:30 am and 15:30 pm when air temperature and PAR were elevated compared to the early morning and evening sampling events. More data points between these times would permit better characterization of any winter diurnal trend in CH_3Br fluxes at this site. As observed in the summer, CH_3Cl fluxes did not follow a well-defined diurnal trend. The switching between net uptake and net emission of CH_3Br is consistent

with bidirectional soil-associated uptake and plant-associated emission processes occurring at this wetland throughout winter. Plant-associated CH_3Br emission was dominant at higher temperature and PAR intensity, but soil-associated uptake, not normally observed at this site, was apparent when the plants were less active.

[31] The absence of consistent diurnal trends across all wetland sites suggests that CH_3X flux is not dominated by fundamental photosynthetic pathways within the plant, but is likely a consequence of the heterogeneity of processes contributing to net flux across the diversity of wetland systems investigated (see section 3.6).

3.3. Vegetation Removal Experiments

[32] Figure 3 shows the average net CH_3X fluxes at each wetland site before, immediately after, and two weeks after removal of vegetation from each sampling point. No CH_3Cl data were available for the vegetation removal experiment at OCF due to analytical problems. CH_3Br emissions stopped

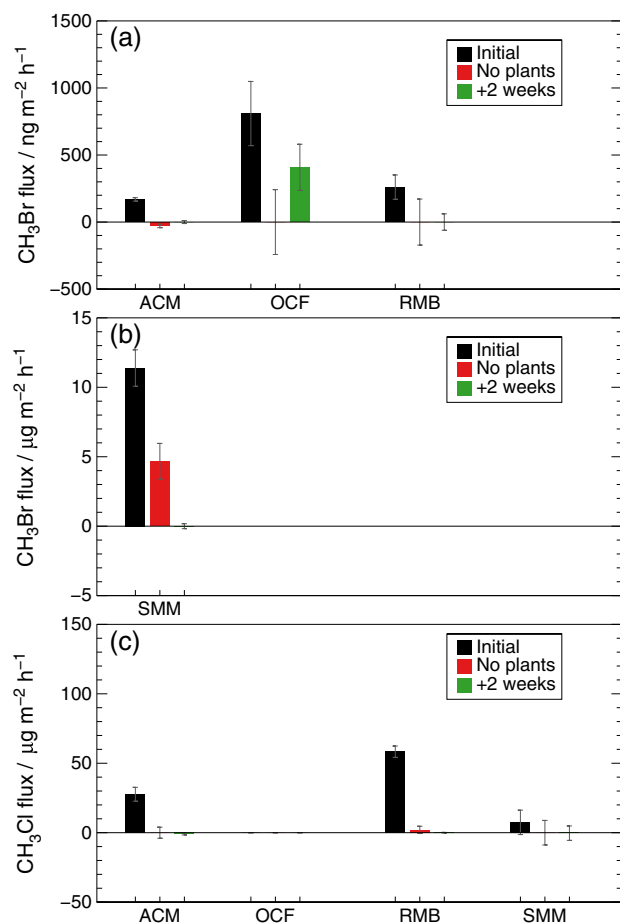


Figure 3. Mean net fluxes of (a) CH₃Br at ACM, OCF, and RMB; (b) CH₃Br at SMM; and (c) CH₃Cl at ACM, RMB, and SMM (no CH₃Cl data at OCF because of instrumentation failure), before vegetation removal (black bars), immediately after vegetation removal (red bars) and two weeks after vegetation removal (green bars). The error bars show the average analytical uncertainty in the fluxes at the individual sampling points in a wetland, including for the instances where average net flux was zero.

or were significantly reduced immediately after vegetation removal at ACM1, ACM4, OCF1-3, OCF5, and RMB1-3, while CH₃Cl emissions stopped or were significantly reduced immediately after vegetation removal at ACM2, ACM4, RMB1-3, RMB6-7, SMM1, and SMM3. These sampling points had generally been strong emitters of CH₃Br and/or CH₃Cl. After two weeks no significant CH₃Br or CH₃Cl emissions were observed at any of the sampling points. The measurements after vegetation removal showed that the wetland sites studied here were not large sinks for CH₃X, in concordance with results from vegetation removal experiments in New Hampshire peatlands [White *et al.*, 2005] and Scottish salt marshes [Blei *et al.*, 2010b].

[33] At the SMM reed wetland, the CH₃Br emissions continued immediately after the vegetation was removed, although at SMM1-3 these emissions were significantly less than prior to vegetation removal. CH₃Br emissions from all SMM sampling points had ceased 2 weeks later. The reduction in emissions immediately after vegetation removal suggests that CH₃Br was mainly produced by the above-ground

parts of the *P. australis* plants. The lower, but significant, emission after vegetation removal indicates that CH₃Br was also produced below-ground prior to transportation to the surface via the *P. australis* stems. It seems likely that the rhizomes and/or root of the *P. australis* were responsible for subsurface CH₃Br production. The absence of emissions after two weeks suggests that the subsurface plant contribution eventually died following removal of the photosynthesizing leaves and stems.

3.4. Environmental Drivers of CH₃Br and CH₃Cl Fluxes

[34] Figure 1 shows that CH₃X emissions broadly corresponded to annual trends in temperature and PAR intensity, consistent with a vegetation origin. However, there did not appear to be a “threshold” temperature (air or soil) or PAR intensity that triggered onset or cessation of CH₃X emissions. Seasonally-defined net CH₃X uptake (CH₃Br only) was only observed at ACM (Figure 1b), likely after CH₃Br emissions had sufficiently reduced. Thus, the apparent onset of CH₃Br uptake coincided with decreasing temperature and PAR intensity in September. A soil-associated uptake process is likely to depend specifically on soil temperature [Hines *et al.*, 1998] rather than air temperature or PAR intensity. Hence, the slower decline of soil temperature compared to air temperature may have allowed CH₃Br uptake to continue at ACM into the early winter months.

[35] To investigate potential drivers of seasonal variation in CH₃X fluxes, correlations were calculated between fluxes and air temperature, soil temperature, PAR intensity, and soil water-level (Table 2). Measurements of zero flux were excluded in the calculations. The correlation between CH₃X emissions and the environmental parameters was generally better than the correlation between the environmental parameters and CH₃X uptake. However, none of the measured environmental parameters was a consistent driver of CH₃Br uptake or emission across the wetland sites. CH₃Cl emission was positively correlated with air temperature at OCF ($r=0.54$), RMB ($r=0.40$), and SMM ($r=0.57$), while CH₃Br and CH₃Cl emissions were positively correlated with soil temperature at OCF ($r_{\text{CH}_3\text{Cl}}=0.56$, $r_{\text{CH}_3\text{Br}}=0.40$) and SMM ($r_{\text{CH}_3\text{Cl}}=0.48$, $r_{\text{CH}_3\text{Br}}=0.51$). The correlation between soil temperature and CH₃X flux at SMM likely reflects the annual life cycle of the *P. australis* plants at SMM, which regrow each year from subsurface rhizomes. For this species, soil temperature appears to be the most important driver of CH₃Br emission, but CH₃Cl fluxes were also positively correlated with soil water level and air temperature. PAR intensity was only positively correlated with CH₃Cl flux at OCF and RMB. These observations further suggest that although CH₃X emission is a plant-based process, it is not directly linked to primary photosynthetic pathways. It is not understood why CH₃Br emissions at ACM were so strongly negatively correlated with PAR intensity.

[36] Soil water level was negatively correlated with CH₃Br emission at ACM and with CH₃Cl emission at ACM and RMB. Here negative correlation indicates greater emission at lower water table. The water level at ACM and RMB reflects microtopographical features at these two wetlands. CH₃Br emissions at ACM were predominantly from ACM4, which enclosed similar vegetation to ACM1, but was sited at a higher point in the peat bog where the water level and peat water content were consistently lower

Table 2. Pearson Correlation Coefficients Between Methyl Halide Fluxes and Environmental Parameters at Auchencorth Moss (ACM), Old Castles Farm (OCF), Red Moss of Balerno (RMB) and St. Margaret's Marsh (SMM) Wetlands^a

	Net Emission								Net Uptake							
	CH ₃ Br				CH ₃ Cl				CH ₃ Br				CH ₃ Cl			
	ACM	OCF	RMB	SMM	ACM	OCF	RMB	SMM	ACM	OCF	RMB	SMM	ACM	OCF	RMB	SMM
<i>T</i> air	-0.30	0.27	0.32	0.21	0.27	0.54	0.40	0.57	-0.02	b	b	b	-0.02	-0.28	b	-0.17
<i>T</i> soil	0.01	0.40	0.04	0.51	0.23	0.56	0.28	0.48	0.13	b	b	b	-0.29	-0.36	b	-0.19
Water level	-0.42	-0.17	-0.35	-0.36	-0.45	0.01	-0.52	-0.08	-0.30	b	b	b	0.33	-0.39	b	0.33
PAR	-0.77	-0.05	0.32	0.15	-0.01	0.64	0.33	0.69	0.30	b	b	b	-0.22	-0.77	b	-0.18

^aBold indicates significant at $p < 0.05$.^b(a) No significant CH₃Br or CH₃Cl uptake at these wetlands. (b) Insufficient data points to quantify correlation.

(Table 1). At RMB, CH₃Br emissions were predominantly from the sampling points enclosing *C. vulgaris*, which were situated in the raised ombrotrophic area of the peat bog where the peat water level was consistently lower. In contrast, the plants situated in the lower, wetter areas of the bog at ACM1-2 emitted much less CH₃Br (Table 1).

[37] The general absence of any correlation between CH₃X uptake and the environmental parameters may at least in part reflect the few observations of net uptake in this study.

[38] As a general observation there were stronger positive associations of net emissions with temperature and lower water table than with PAR, i.e., to variables that have longer (seasonal) time constants through their range of variability (cf. PAR intensity which has very short time-constant variability). However, it is intrinsically difficult to isolate the effect of individual parameters in a complicated ecosystem. Different parameters may affect different methyl halides and different processes differently, as well as being inherently confounded. For example, a sunny summer day is also likely to be warm. Further confounding may also arise from plants emitting variable amounts of CH₃X at different stages of their growth cycles such as flowering and seeding, as observed in rice plants [Redeker *et al.*, 2002], where CH₃Br emissions increased until the start of the reproductive stage, were variable during the reproductive stage and declined thereafter. Even studies in an environment where temperature, light intensity and water level are tightly controlled and manipulated would likely struggle to separate out the myriad of potential interacting factors.

3.5. CH₃X Fluxes at Caerlaverock Wetland

[39] The average CH₃X fluxes measured on four occasions at the additional Caerlaverock (CLR) *P. australis* wetland are compared in Figure 4 with the CH₃X fluxes measured at similar times of year at the similar SMM wetland. CH₃Cl measurements were not undertaken prior to January 2008. The average CH₃Br flux (± 1 SD) from $n=29$ measurements at CLR was 1610 ± 920 ng m⁻² h⁻¹. The CH₃Cl fluxes from CLR were not significant and are not discussed further.

[40] CH₃Br emissions were observed from CLR in August 2007, May 2008, and July 2009, which were within the growing season, but not in November 2007, which fell outside the growing season. These observations are consistent with the annual trends observed in CH₃Br fluxes at SMM (Figure 1k), although the limited number of sampling events at CLR clearly limits detailed analysis of annual trend. On average the CH₃Br emissions from CLR were smaller than those from SMM (Figure 4), but the *P. australis* plants at

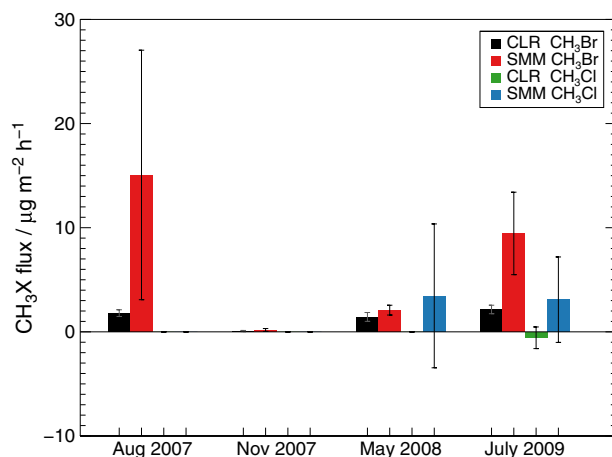


Figure 4. Mean CH₃X net fluxes from the St Margaret's Marsh (SMM) and Caerlaverock (CLR) *P. australis* wetlands on four measurement occasions between August 2007 and July 2009. Uncertainty bars show ± 1 SD where $n=4$ for measurements at SMM on 30 August 2007, 18 October 2007, 21 May 2008, and 07 July 2009, and $n=8, 6, 3$, and 11 for measurements at CLR on 23 August 2007, 09 November 2007, 05 May 2008, and 21 July 2009, respectively. At these wetlands the CH₃Br and CH₃Cl fluxes were of similar magnitude and are plotted on a common scale. No CH₃Cl measurements were made in 2007.

CLR were shorter than at SMM. The CH₃Br fluxes normalized to *P. australis* biomass enclosed within eight sampling points at the two wetlands are given in Table 3 and are remarkably consistent for CLR1-4 and SMM2-4, in the range 2–4 ng (g fwt)⁻¹ h⁻¹. It is important to note that fluxes normalized to biomass represent only a “snapshot”, because

Table 3. Comparison of CH₃Br Fluxes at Four Sampling Points at St Margaret's Marsh (SMM) and Caerlaverock (CLR) *P. australis* Wetlands^a

	CH ₃ Br Flux / ng (g Dry Weight) ⁻¹ h ⁻¹	
	SMM	CLR
1	11.7 (± 0.4)	2.3 (± 0.2)
2	4.0 (± 0.3)	3.5 (± 0.2)
3	2.0 (± 0.1)	4.1 (± 0.3)
4	2.0 (± 0.2)	3.0 (± 0.1)

^aFluxes are expressed per mass of above-ground *P. australis* present at the final flux measurement. Because only one flux determination is available at each sampling point, the analytical uncertainty in the measurement is presented.

vegetation removal to determine mass could only be undertaken once at each sampling point. Although SMM and CLR were both close to the coast, with higher soil halogen concentrations than at the other wetlands (Table 1), the CH_3Br fluxes normalized to biomass were also similar at sampling point OCF5, an inland wetland site with *P. australis* (Table 1), indicating that *P. australis* is a consistently strong emitter of CH_3Br .

3.6. Heterogeneity in CH_3X Fluxes and a Dominant Role for Plant Species

[41] Within each wetland the net fluxes from the individual sampling points varied in magnitude and direction (Table 1). For example, at ACM the net CH_3Br and CH_3Cl emissions from ACM4 were comparatively large and followed well-defined seasonal trends. In contrast, CH_3Br and CH_3Cl emissions from ACM1-3 were small and did not follow distinct seasonal trends. At RMB, particularly large CH_3Br and CH_3Cl emissions, with well-defined annual trends, were observed at RMB1-3, but the CH_3X fluxes from RMB4 were small and variable (Table 1). There was insufficient data to elucidate seasonal trends at RMB5-7, but the limited measurements showed high CH_3Br and CH_3Cl fluxes from RMB6 and much smaller fluxes at RMB5 and RMB7-8.

[42] The variability in subdiurnal CH_3X net fluxes and in the associations of fluxes with environmental parameters also supports substantial heterogeneity in the factors contributing to the observed net flux at a given location and time. This considerably complicates the formulation of general predictive conclusions for CH_3X net fluxes from these ecosystems, and hence in an extrapolation to global scale. Nevertheless, several observations from this study demonstrate that intersite and intrasite heterogeneity in CH_3X fluxes from the four wetlands was primarily influenced by vegetation cover.

[43] First, where sampling points within a wetland had similar species composition, the CH_3X fluxes and annual trends were similar, irrespective of differences in microtopography between the sampling points. This was clearly demonstrated at SMM and RMB. CH_3Br emissions were consistently large (and had annual cycle) at SMM1-4 where only *P. australis* was present in both wetter (SMM1-2) and drier (SMM3-4) areas of the wetland (Table 1). CH_3Br and CH_3Cl emissions were also seasonally well-defined and consistently large at RMB1-3, which predominantly enclosed *C. vulgaris* (Table 1) in locations that encompassed ombrotrophic and minerotrophic areas at either hummocks or hollow sites.

[44] Second, where sampling points were similar in their microtopography, CH_3X fluxes only differed if the vegetation was dissimilar. This was best demonstrated at RMB where eight sampling points gave greater spatial coverage. RMB1, RMB5, and RMB6 were all situated on hummocks in the ombrotrophic part of the bog, and RMB3 and RMB8 were situated on hummocks in the minerotrophic area of the bog. Large CH_3X fluxes were only observed from RMB1, RMB3, and RMB6, which predominantly enclosed *C. vulgaris* (Table 1).

[45] Third, if the same species was present at sampling points located in different wetlands, the CH_3X fluxes were similar in magnitude and showed similar seasonal trends, as exemplified by large CH_3Br emissions from the *P.*

australis sampling points at OCF5, SMM1-4 (Table 1), and CLR (Figure 4).

[46] These observations concur with studies in peatlands [Dimmer *et al.*, 2001] and salt marshes [Manley *et al.*, 2006; Blei *et al.*, 2010b] in which plant species was reported to be the major driver of heterogeneity in CH_3Br and CH_3Cl fluxes, and also with results from surveys of Malaysian [Saito *et al.*, 2008; Blei *et al.*, 2010a] and Japanese [Yokouchi *et al.*, 2007] tropical plants where the magnitude of CH_3Cl emissions depended greatly on the species.

[47] At sampling points that enclosed a single species, or a very large proportion of a single species, the origin of the CH_3X emissions was easily pinpointed, e.g., *P. australis* at SMM1-4 and *C. vulgaris* at RMB1-3 (Table 1). The origin of CH_3Br and CH_3Cl emissions from sampling points enclosing a variety of species, such as ACM4, was less clear. ACM4 enclosed similar vegetation to ACM1 (Table 3), but had much higher CH_3X emissions, possibly as a result of confounded microtopological and environmental effects. At sampling points where there was mixed vegetation, a more detailed vegetation removal experiment, where one species was removed at a time, could help CH_3X source(s) to be more accurately identified.

[48] *P. australis* and *C. vulgaris* emitted large amounts of CH_3Br and/or CH_3Cl per unit area in comparison to CH_3X emissions previously observed at peatland sites [Varner *et al.*, 1999a; Dimmer *et al.*, 2001; White *et al.*, 2005]. However, area fluxes do not account for the mass of vegetation within the sampling point, which was much larger at the SMM sampling points compared with, for example, the ACM sampling points. CH_3X fluxes expressed in $\text{ng (g dwt)}^{-1} \text{h}^{-1}$ are shown in Table 1. The highest CH_3Br emissions per unit biomass were observed from *P. australis* plants. High CH_3Br emissions per unit biomass were observed from OCF2-3 and high CH_3Cl emissions per unit biomass were observed from RMB1 and RMB3. No fluxes were observed from RMB2 and RMB6 on the day of sampling. Despite high area-based CH_3Br emissions from RMB1 and RMB3, the emissions as a function of dry mass were small reflecting the denser, woody *C. vulgaris* at these sampling points.

[49] The most likely plant CH_3X production mechanism is methyl transferase catalysis of halide methylation via *S*-adenosyl methionine [Saini *et al.*, 1995; Attieh *et al.*, 1995]. Heterogeneity in CH_3X emissions between species indicates that this pathway could be more or less active in different plant species. In species such as *P. australis* where CH_3Br emissions per unit area and per unit mass were uniformly high across different wetland sites (Old Castles Farm, St Margaret's Marsh and Caerlaverock), CH_3Br production pathways appear particularly active. For *P. australis* this is likely a direct result of this species' propensity to thrive in brackish water, as at St. Margaret's Marsh and Caerlaverock, and to accumulate Br^- in both root and leaf tissue [Xu *et al.*, 2004]. At many of the individual sampling points there were marked differences between CH_3Br and CH_3Cl fluxes (Table 1 and Figure 1), which were not significantly correlated at any of the Scottish wetlands. At many sampling points CH_3Br emissions were of similar magnitude or greater (SMM sampling points) than the CH_3Cl emissions, despite the greater abundance of Cl^- compared with Br^- (Table 1). This finding is in agreement with observations at Scottish salt marshes [Blei *et al.*, 2010b] and is suggested

to be due to the greater nucleophilicity of Br^- in the methyl transferase reaction compared with Cl^- .

4. Estimation of Global Importance of CH_3X Fluxes From Wetlands

[50] It is difficult to estimate global terrestrial fluxes of CH_3X because of (a) uncertainties in extrapolating spatial and temporal point measurements of fluxes to all such ecosystems and times, and (b) uncertainties in global land cover area estimates. *WMO* [2011] currently reports estimates for global fluxes from wetlands of 0.6 Gg yr^{-1} for CH_3Br and 48 Gg yr^{-1} for CH_3Cl ; the former value is stated by *WMO* [2011] to be a downward revision from a previous reported wetlands CH_3Br flux of 4.6 Gg yr^{-1} . The *WMO* global estimates are derived only from measurements made in peatland-type wetlands in Ireland [Dimmer *et al.*, 2001] and New Hampshire [White *et al.*, 2005]. It should also be noted that Dimmer *et al.* [2001] tentatively estimated total wetland source strengths (including fluxes from forested bog sites) of 5.0 Gg yr^{-1} CH_3Br and 34.7 Gg yr^{-1} CH_3Cl , indicating that the *WMO* CH_3Br source may not reflect emissions from freshwater wetlands as a whole.

[51] In this section, we provide different estimates of global wetland CH_3X net fluxes by combining CH_3X flux data from a number of different freshwater wetland ecosystems including peatland, nonpeatland, and high latitude. We also use two separate sets of estimates of global areas of different types of freshwater wetlands in order to highlight the effect on global flux estimates of uncertainties in these data. Both of the following estimates for global wetland area include freshwater wetlands only; anthropogenic wetlands (e.g., rice paddies) and marine wetlands (e.g., salt marshes and mangrove swamps) are not included:

1. Matthews and Fung [1987] estimated a global freshwater wetland area of $5.3 \times 10^6 \text{ km}^2$ from three independent digital sources: (a) vegetation cover, (b) soil properties, and (c) fractional inundation in $1^\circ \times 1^\circ$ lat-long grid cells. This dataset provides the latitudinal distribution of five major wetland groups classified according to vegetation cover: forested bog, nonforested bog, forested swamp, nonforested swamp, and alluvial formations.
2. Lehner and Doll [2004] estimated a global freshwater wetland area of $6.07\text{--}8.03 \times 10^6 \text{ km}^2$ distributed across six categories: freshwater marsh/flood plain, swamp forest/flooded forest, bog/fen/mire, "wetland complex", "25–50% wetland", and "50–100% wetland." The latter three classifications refer to fractional wetland areas; specifically "wetland complex" is a mix of wetland types for which a clear spatial coverage ratio could not be identified. The range of $6.07\text{--}8.03 \times 10^6 \text{ km}^2$ reflects the different interpretations of the fractional wetland classes. Area corresponding to lake, reservoir, river, coastal wetlands, and pan/brackish/saline wetland classes was not included in the total global wetland area quoted here. A third literature estimate of $3.46 \times 10^6 \text{ km}^2$ from Gorham, 1991 was not used in this study because it refers only to boreal and Arctic peatlands.

[52] For each wetland site in this study, mean annual emission and uptake were calculated. Mean annual emissions

(and/or uptake) were determined from measurements of positive (and/or negative) net flux averaged over the number of days for which net emission (and/or uptake) was observed at the wetland site (~ 240 days for the wetlands in this study). If no net emission flux was observed during the total sampling period, the mean annual flux was $0 \text{ g m}^{-2} \text{ yr}^{-1}$, e.g., for CH_3Br uptake at St Margaret's Marsh. Mean annual fluxes for emission and uptake are presented in Table 4 together with flux data from Irish peatlands [Dimmer *et al.*, 2001], New Hampshire peatlands [White *et al.*, 2005], high-latitude Swedish wetlands [Hardacre *et al.*, 2009], and Alaskan tundra [Teh *et al.*, 2009]. The average annual CH_3X fluxes from the Scottish wetland site were, in general, greater in magnitude than the fluxes from Irish and New Hampshire peatlands. Two estimates of global CH_3X fluxes were derived (Table 5) by assigning the wetland types in Table 4 among the different categories of wetlands listed by Matthews and Fung [1987] and Lehner and Doll [2004], and multiplying the mean annual flux for that wetland type (or the average across the assigned wetland types, if more than one) by the estimated global wetland area for that category. The assignment was made according to which of the data in Table 4 best matched a category description. For example, for the "forested bog" wetland class, an average of the mean annual fluxes from ACM, RMB, New Hampshire and Irish bogs was used. Where no mean annual flux for a wetland class was available, e.g., forested swamps, an average flux value was used. Lehner and Doll [2004] present lower and higher estimates of global wetland area for the "50–100% wetland", "25–50% wetland", and "wetland complex" classes. The higher estimates for area and resulting fluxes are also presented (in brackets) in Table 5.

[53] The net flux estimates presented in Table 5 are in the range $14\text{--}42 \text{ Gg yr}^{-1}$ CH_3Br and $740\text{--}1100 \text{ Gg yr}^{-1}$ CH_3Cl depending on global land area estimates used. These are very considerably larger than the *WMO* [2011] estimate of 0.6 Gg yr^{-1} CH_3Br and 48 Gg yr^{-1} CH_3Cl , although as noted above the 0.6 Gg yr^{-1} flux for CH_3Br is a downward revision from a previous value of 4.6 Gg yr^{-1} , this latter estimate being not so very different from the lower of the estimates derived in this work for CH_3Br . The estimates in Table 5 represent up to $\sim 20\%$ of current estimated sinks for each of CH_3Br and CH_3Cl compared with the $\sim 1\%$ proportion currently assigned to peatlands [WMO, 2007; WMO, 2011]. The greater fluxes reported here reflect: (1) the large CH_3Br emissions from *P. australis* in reed beds and the large CH_3Cl emissions from *C. vulgaris* in peatlands—measurements from these systems have not been made before, but in this work these large emissions were prevalent over more than a year of sampling and at different sampling points; (2) the year-round active period for CH_3X emissions at certain sampling sites (OCF and RMB). It is also not clear the extent to which the *WMO* global values encompass all the types of peatlands/wetlands considered in the scale-up presented in Table 5. Although wetlands are not a separate CH_3X sink in the *WMO* [2011] budgets (the uptake observed in Scottish wetlands was likely soil-associated uptake processes), it is important to note that wetland soils do contribute to global CH_3X uptake. The CH_3Br and CH_3Cl sinks calculated here are a very small percentage of the global soil sinks, but the estimate of -5.6 Gg yr^{-1} CH_3Br uptake (scenario 1)

Table 4. Comparison of Estimated Mean Annual CH₃Br and CH₃Cl Fluxes From Scottish, Irish, New Hampshire (USA) and High Latitude (Arctic Sweden) Wetlands, and Alaskan Arctic Tundra

	CH ₃ X Flux / g m ⁻² yr ⁻¹ (Active Period)								
	ACM	OCF	RMB	SMM	Irish Peatlands	New Hampshire Peatlands ^a	High Latitude Wetlands ^b	Arctic Tundra ^a	Overall Average
CH ₃ Br emission	1.8 × 10 ⁻⁴	3.1 × 10 ⁻³	3.8 × 10 ⁻³	0.017	9 × 10 ⁻⁴ (4.8 × 10 ⁻³)	6 × 10 ⁻⁵	2.9 × 10 ⁻⁵	1.52 × 10 ⁻⁴	3.8 × 10 ⁻³
CH ₃ Br uptake	-1.2 × 10 ⁻⁴	0.0	-3.5 × 10 ⁻⁵	0.0	No data	-1.5 × 10 ⁻⁴	-3.2 × 10 ⁻³	-6.82 × 10 ⁻⁴	-8.4 × 10 ⁻⁴
CH ₃ Cl emission	0.043	6.2 × 10 ⁻³	1.5	7.1 × 10 ⁻³	5.3 × 10 ⁻³ (0.033)	0.014	4.1 × 10 ⁻³	1.60 × 10 ⁻³	0.31
CH ₃ Cl uptake	-6.1 × 10 ⁻³	-2.9 × 10 ⁻³	0.0	-0.010	No data	0.0	-8.5 × 10 ⁻⁵	-1.46 × 10 ⁻²	-3.9 × 10 ⁻³

^aAverage annual fluxes from Irish peatlands calculated from estimates of 0.9 Gg yr⁻¹ CH₃Br and 5.5 Gg yr⁻¹ CH₃Cl with a global peat bog area of 1.04 × 10⁶ km² [Dimmer et al., 2001]. Values in brackets are tentative annual fluxes from a total wetland source calculated from estimates of 5.0 Gg yr⁻¹ CH₃Br and 34.7 Gg yr⁻¹ CH₃Cl and a global wetland area of 5.3 × 10⁶ km² [Dimmer et al., 2001].

^bAverage annual CH₃Br emissions were calculated from the seasonal measurements of net emission made at two sampling sites [White et al., 2005]. Average annual CH₃Br uptake was similarly calculated from the seasonal measurements of net uptake. Measurements from the vegetation removal experiment are not included. A 240 day growing season is assumed [Varner et al., 1999a]. Average annual fluxes of CH₃Cl calculated from a source strength of 48 Gg yr⁻¹ and a global wetland area of 3.56 × 10⁶ km² [Varner et al., 1999a].

^cAverage annual fluxes calculated using a 24 h daily emission period and a 100 day growing season [Hardacre et al., 2009].

^dAverage annual CH₃Br and CH₃Cl emission and uptake were calculated from the gross fluxes reported by Teh et al. [2009] assuming a 100 day growing season.

represents ~1.5% of the total CH₃Br sink strength [WMO, 2011]. This figure was driven by uptake at ACM and high latitude wetlands.

[54] These estimates highlight how global scale-up is crucially sensitive to land-cover definition and to the uncertainties associated with using a “bottom up” approach to assignment of appropriate flux values. For example the smaller global CH₃Br flux of 14 Gg yr⁻¹ in scenario 1 compared with 35 (or 42) Gg yr⁻¹ CH₃Br in scenario 2 was the result of (a) defining a separate high-latitude wetland area and using mean annual flux derived specifically from high-latitude wetlands, and (b) the larger area defined as bog for which the high mean annual fluxes from SMM were not taken into account.

[55] Unless there are many species that emit as strongly as *C. vulgaris* and *P. australis*, it is likely that global wetland CH₃Br and CH₃Cl emissions are overestimated here. Indeed, model predictions of a large tropical biogenic CH₃Cl source [Lee-Taylor et al., 2001; Yoshida et al., 2004; Yoshida et al., 2006; Xiao et al., 2010], which have been partially substantiated by limited field measurements [Gebhardt et al., 2008; Yokouchi et al., 2002; Yokouchi et al., 2007; Blei et al., 2010a], rather than a greatly increased temperate latitude source, will likely more closely balance the CH₃Cl budget. Nevertheless, *C. vulgaris* and *P. australis* are prevalent in middle- to high-latitude wetlands so this work provides a strong indicator that global emissions for CH₃Br and CH₃Cl from wetlands as a whole (i.e., peatlands and other freshwater wetland systems) are likely currently underestimated for both CH₃Br and CH₃Cl. The data from this study are derived from measurements at middle- to high-latitude peatlands and wetlands. To date there have been no investigations of CH₃X in tropical to midlatitude wetlands, and these systems need to be studied to obtain a better picture of wetland CH₃X fluxes globally.

5. Conclusions

[56] The results presented here describe CH₃Br and CH₃Cl fluxes in wetlands in greater detail than has previously been reported. All five Scottish wetlands emitted CH₃Br and/or CH₃Cl on average, overall, although some individual sampling locations were small sinks of one or other methyl halide. Where sampling points within the Scottish wetlands emitted substantial amounts of CH₃Br and CH₃Cl, these emissions followed clear seasonal trends with the greatest emissions of CH₃Br and CH₃Cl observed in early summer. Seasonal patterns in CH₃Br and CH₃Cl fluxes were linked to seasonal patterns in air temperature, soil temperature, and PAR intensity through the annual plant growth cycle, but sample-by-sample variation in CH₃Br and CH₃Cl fluxes was not strongly linked to any of the measured environmental parameters individually. Some daily cycles in CH₃Br and CH₃Cl fluxes were observed but these were not consistent.

[57] CH₃Br and CH₃Cl emissions were strongly associated with plant species and two species in particular, *Calluna vulgaris* and *Phragmites australis*, emitted large quantities of CH₃Br. *C. vulgaris* also emitted large amounts of CH₃Cl, which continued, together with the CH₃Br emissions, throughout winter, albeit at lower rates. Measurements following vegetation removal showed that the wetland sites

Table 5. Estimates of Global Annual CH_3Br and CH_3Cl Fluxes Derived From Mean Annual CH_3Br and CH_3Cl Fluxes Scaled up With Two Estimates of Global Areas of Different Types of Wetlands^a

Wetland Class	CH ₃ Br Source Flux		CH ₃ Br Sink Flux		CH ₃ Cl Source Flux		CH ₃ Cl Sink Flux	
	Area / m ²	/ g m ⁻² yr ⁻¹	/ g m ⁻² yr ⁻¹	/ Gg yr ⁻¹	/ g m ⁻² yr ⁻¹	/ Gg yr ⁻¹	/ g m ⁻² yr ⁻¹	/ Gg yr ⁻¹
<i>Scenario 1</i>								
Forested bog ^a	1.15 × 10 ¹²	1.64 × 10 ⁻³	1.88	1.02 × 10 ⁻⁴	-0.17	3.91 × 10 ⁻¹	-2.03 × 10 ⁻³	-2.33
Nonforested bog ^a	3.91 × 10 ¹¹	1.64 × 10 ⁻³	0.64	-1.02 × 10 ⁻⁴	-0.04	3.91 × 10 ⁻¹	-2.03 × 10 ⁻³	-0.80
Forested swamp ^b	1.08 × 10 ¹²	3.83 × 10 ⁻³	4.13	-5.03 × 10 ⁻⁴	-0.54	2.01 × 10 ⁻¹	-3.30 × 10 ⁻³	-3.56
Nonforested swamp ^c	9.81 × 10 ¹¹	1.01 × 10 ⁻²	9.86	0.00	0.00	6.65 × 10 ⁻³	-6.45 × 10 ⁻³	-6.33
Alluvial formations ^b	1.95 × 10 ¹¹	3.83 × 10 ⁻³	0.75	-5.03 × 10 ⁻⁴	-0.10	2.01 × 10 ⁻¹	-3.30 × 10 ⁻³	-0.64
Wetland 60°N–90°N ^d	1.47 × 10 ¹²	3.54 × 10 ⁻⁵	0.05	-1.61 × 10 ⁻³	-2.37	1.83 × 10 ⁻³	-2.04 × 10 ⁻³	-3.00
Total area / m ²	5.26 × 10 ¹²							
Total / Gg yr ⁻¹			17.3		-3.2	866		-16.7
Net Flux / Gg yr ⁻¹				14				850
<i>Scenario 2</i>								
Freshwater marsh/ floodplain ^e	2.53 × 10 ¹²	1.01 × 10 ⁻²	25.4	0.00	0.00	6.65 × 10 ⁻³	-6.45 × 10 ⁻³	-16.3
Swamp forest/flooded forest ^b	1.17 × 10 ¹²	3.83 × 10 ⁻³	54.46	-5.03 × 10 ⁻⁴	-0.59	0.20	-3.30 × 10 ⁻³	-3.84
Bog/fen/mire ^a	7.08 × 10 ¹¹	1.12 × 10 ⁻³	0.979	-8.37 × 10 ⁻⁴	-0.59	0.26	-4.16 × 10 ⁻³	-2.95
50%–100% wetland ^b	8.82 × 10 ¹¹	3.83 × 10 ⁻³	3.38	-5.03 × 10 ⁻⁴	-0.44	0.20	-3.30 × 10 ⁻³	-2.91
25%–50% wetland ^b	(1.76 × 10 ¹²)	3.83 × 10 ⁻³	(6.76)	-5.03 × 10 ⁻⁴	(-0.89)	(355)	-3.30 × 10 ⁻³	(-5.50)
Wetland complex ^b	7.90 × 10 ¹¹	3.83 × 10 ⁻³	3.03	-5.03 × 10 ⁻⁴	-0.40	159	-3.30 × 10 ⁻³	-2.61
	(1.58 × 10 ¹²)		(6.05)		(-0.80)	(318)		(-5.21)
	0.00		0.00		0.00	0.00		0.00
	(2.88 × 10 ¹¹)		(1.10)		(-0.15)	(57.9)		(-0.95)
Total area / m ²	6.07 × 10 ¹²							
	(8.03 × 10 ¹²)							
Total / Gg yr ⁻¹			37.1 (44.6)		-2.02 (-3.01)	772 (1170)		-28.0 (-35.0)
Net Flux / Gg yr ⁻¹				35 (42)				743 (1130)

^aScenario 1: Global wetland areas from *Matthews and Fung* [1987], Scenario 2: Global wetland areas from *Lehner and Doll* [2004]. Using the lower of these authors' two area estimates for the categories "50–100% Wetland", "25–50% Wetland", and "Wetland Complex"; Values using the higher of the two area estimates for these categories are given in brackets. The fluxes in g m⁻² yr⁻¹ for the different classes are derived from the values given in Table 4 combined according to the footnotes to this table.

^bAverage flux for forested bog and nonforested bog derived from ACM, RMB, New Hampshire, Ireland (bog only) values.

^cAverage flux for forested swamp, alluvial, 50–100% wetlands, 25–50% wetlands and wetland complexes derived from ACM, OCF, RMB, SMM, New Hampshire, Ireland (total) values.

^dAverage flux for nonforested swamp, freshwater marsh/floodplain, swamp forest/flooded forest derived from OCF and SMM values.

^eAverage flux for wetlands 60°N–90°N derived from high latitude wetlands value.

^fAverage flux for bog/fen/mire derived from ACM, RMB, New Hampshire, Ireland (bog only), high latitude values.

studied here were not large sinks for CH_3Br or CH_3Cl . On average CH_3Br and CH_3Cl net fluxes from these Scottish wetlands were generally larger and observed over a longer period than has been observed previously in temperate wetland ecosystems. However, the relevance of applying these emissions globally is difficult to quantify because of great uncertainties in relevant land-cover estimates and in the validity of extrapolation spatially—but this is the case for any similar study. Nevertheless, the observations in this study suggest that some temperate wetlands emit more CH_3Br and CH_3Cl to the atmosphere than previously estimated and that the current global source strengths for both methyl halides from these ecosystems are likely underestimated.

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